

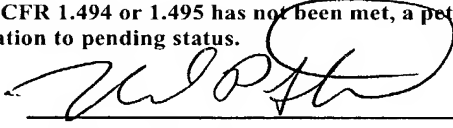
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<b>BAKER BOTTS LLP</b> TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35.U.S.C. 371		EXPRESS MAIL LABEL No EU 206 385 477	DATE March 7, 2002
		ATTORNEY'S DOCKET NO A35043-PCT-USA	
		U.S. APPLICATION NO <b>10/070477</b>	
INTERNATIONAL APPLICATION NO PCT/KR00/00956	INTERNATIONAL FILING DATE August 25, 2000	PRIORITY DATE CLAIMED September 7, 1999	
TITLE OF INVENTION <b>POLYMER FOR CHEMICALLY AMPLIFIED RESIST AND A RESIST COMPOSITION USING THE SAME</b>			
APPLICANT(S) FOR DO/EO/US <b>Deog-Bae KIM, Hyun-Jin KIM, Yong-Joon CHOI, and Yoon-Sik CHUNG</b>			
<p>Applicant herewith submits to the United States Designated /Elected Office (DO/EO/US) the following items and other information:</p> <ol style="list-style-type: none"> <li><input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.</li> <li><input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.</li> <li><input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(I).</li> <li><input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19<sup>th</sup> month from the earliest claimed priority date.</li> <li><input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))             <ol style="list-style-type: none"> <li><input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</li> <li><input type="checkbox"/> has been transmitted by the International Bureau.</li> <li><input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li><input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</li> <li><input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210)             <ol style="list-style-type: none"> <li><input checked="" type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</li> <li><input type="checkbox"/> have been transmitted by the International Bureau</li> <li><input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li><input type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li><input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li><input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</li> <li><input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</li> </ol> <p><b>Items 11. to 16. below concern other document(s) or information included:</b></p> <ol style="list-style-type: none"> <li><input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409)</li> <li><input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li><input type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.</li> <li><input type="checkbox"/> A substitute specification.</li> <li><input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li><input checked="" type="checkbox"/> Other items or information.             <ol style="list-style-type: none"> <li><input type="checkbox"/> a copy of the International Search Report (PCT/ISA/210)</li> <li><input type="checkbox"/> a copy of the International Preliminary Examination Report (PCT/IPEA/409)</li> </ol> </li> </ol> <p>           PCT Request            PCT/ISA/220            PCT/IB/308            PCT/IPEA/416            WO 01/18603 A2 (specification - 25 pages, claims - 6 pages, and abstract)         </p>			

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INTERNATIONAL APPLICATION NO PCT/KR00/00956		INTERNATIONAL FILING DATE August 25, 2000		PRIORITY DATE CLAIMED September 7, 1999	
17. <input checked="" type="checkbox"/> The following fees are submitted:				CALCULATIONS <small>PTOUSE ONLY</small>	
<b>Basic National Fee (37 CFR 1.492(a)(1)-(5)):</b> Neither international preliminary examination fee (37 CFR 1.482) Nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO (1.492(a)(3)) \$1,040 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO (1.492(a)(5)) \$890.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO (1.492(a)(2)) \$740.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) (1.492(a)(1)) \$710.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$	1,040
Surcharge of \$130.00 for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 C.F.R. 1.492(e)).				\$	
Claims	Number Filed	Number Extra	Rate	\$	
Total Claims	6 -20=	0	X \$ 18.00	\$	0
Independent Claims	2 -3=	0	X \$ 84.00	\$	0
Multiple dependent claim(s) (if applicable)			+ \$280.00	\$	
TOTAL OF ABOVE CALCULATIONS =				\$	1,040
Reduction by 1/2 for filing by small entity, if applicable.				\$	
SUBTOTAL =				\$	1,040
Processing fee of \$130.00 for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
TOTAL NATIONAL FEE =				\$	1,040
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				\$	
TOTAL FEES ENCLOSED =				\$	1,040
				Amt. refunded	\$
				charged	\$
a. <input checked="" type="checkbox"/> A check in the amount of \$ 1040 00 to cover the above fees is enclosed. b. [ ] Please charge our Deposit Account No. 02-4377 in amount of \$ to cover the above fees. A copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-4377. A copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:			 Attorney: Neil P. Sirota		
Neil P. Sirota BAKER BOTTS L.L.P. 30 Rockefeller Plaza New York, New York 10112-4498			PTO Reg: 38,306 March 7, 2002 Date		

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**BAKER BOTTS** LLP

Attorney Docket Number: A35043-PCT-USA

Title: POLYMER FOR CHEMICALLY AMPLIFIED RESIST AND A RESIST COMPOSITION USING THE SAME

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POLYMER FOR CHEMICALLY AMPLIFIED RESIST AND A RESIST  
COMPOSITION USING THE SAME

BACKGROUND OF THE INVENTION

**(a) Field of the Invention**

5           The present invention relates to a polymer for a chemically amplified resist and a resist composition comprising the same. More particularly, the present invention relates to a novel polymer that can be used for a chemically amplified resist composition that can form finer patterns on a substrate in a micro-lithography process suitable for micro-processing of  
10 semiconductors, using a mono wavelength as the light source for light exposure, and which improves post exposure delay (PED) stability and has high resistance against the heat produced by dry etching, and a resist composition using the same.

**(b) Description of the Related Art**

15           The resist composition is generally used in the preparations of large size integrated circuits (LSI) or in high resolution lithography. Recently, resist compositions with high resolution and high sensitivity have been required due to the densification of large size integrated circuits. Such embodiments of microcircuits in semiconductor integrated circuits generally  
20 proceed using a lithography process through which process the microcircuit is constructed by coating resist on a substrate, transcribing patterns on the substrate using a prepared photo mask, and etching the substrate along the

transcribed pattern.

Such lithography processes comprise the following steps: (a) a coating step comprising uniformly coating resist on the surface of a substrate, (b) a soft baking step comprising evaporating the solvent from the coated resist film to adhere the resist film to the surface of the substrate, (c) a light exposure step comprising light exposing the substrate while projecting the circuit pattern on the mask, repeatedly and sequentially using a light source such as ultraviolet light to transcribe the pattern of the mask onto the substrate, (d) a development step comprising selectively removing the part in which chemical properties such as solubility change by the exposure to the light source using development liquid, (e) a hard baking step for adhering more firmly the resist film that remains on the substrate after development, (f) an etching step comprising etching the predetermined part along the pattern on the developed substrate in order to impart the electric properties and (g) a stripping step comprising removing the resist that becomes unnecessary after said etching step.

The speed of high-integration of semiconductor integrated circuits has increased 4-fold for 3 years. Thus, at present, in the field of dynamic random access memory (DRAM), 64 mega bit DRAM and 256 mega bit DRAM are mass-produced, and the development of giga bit DRAM has started.

The conventional 16 mega DRAM used the technology of a 0.5  $\mu$ m circuit line, while 64 mega DRAM uses the technology of a circuit line of 0.3

$\mu\text{m}$  or less, and 256 mega DRAM and giga DRAM requires an ultra micro pattern of less than quarter micro, such as 0.20  $\mu\text{m}$ , 0.18  $\mu\text{m}$ , 0.15  $\mu\text{m}$  depending on the design. In such micro-processing, the light-radiation wavelength moves to extreme ultraviolet. Therefore, there is a need for the development of a new resist that can effectively respond to extreme ultraviolet light.

The resist of the prior art comprising quinonediazide photoactive material and phenol novolac resin cannot satisfy the above-mentioned requirement, because, in such a resist system, there is a large absorption at the wavelength zone of 300 nm or less and thus, when mono wavelength light-exposure of 300 nm or less is conducted, pattern profile is significantly deteriorated. Therefore, there is a need for the embodiment of a stiff pattern in which the pattern profile does not flow.

In order to embody such a pattern profile, an aligner commonly called a stepper is generally used as a light-exposing apparatus. Such light-exposing apparatuses are divided into an apparatus using G line (wavelength 436 nm), I line (wavelength 365 nm) of mercury light, and an apparatus using an excimer laser of mono wavelength KrF (248 nm) and ArF (193 nm) according to the light source. For embodying micro-patterns on the substrate, the resolution value should be small. The resolution value is expressed by the following Rayleigh diffraction limiting equation. Theoretically, since the resolution value becomes smaller as the wavelength of the light source becomes shorter, it is preferable to use a shorter mono

wavelength.

[Diffraction limiting equation]

$$R = \kappa \lambda / NA$$

Wherein,  $\kappa$  is a constant,  $\lambda$  is a wavelength of the light used, and

5 NA is the number of the aperture of the lense.

In order to achieve high resolution of a quarter micron or less, the capacity of degradation of lithography should be improved. For this purpose, it is effective to use a mono wavelength light source having a short wavelength and to increase the aperture number (NA) of the optical  
10 lense of the exposing apparatus.

Accordingly, a resist composition that uses a high-output excimer laser light source so as to respond to the high-resolution tendency of semiconductor integrated circuits is commonly used. This composition is for a KrF and an ArF excimer laser, and high-sensitivity resist systems  
15 introducing the chemical amplification concept are suggested.

A chemically amplified resist produces acid by photolysis due to the irradiation of extreme ultraviolet light. The produced acid degrades the protective group which is partially protected with the aid of heat, and then it reacts with the acid labile polymer to initiate the chain reaction or act as  
20 a catalyst, and thus, one molecule of acid causes a number of bond formation or bond degradation reactions. Therefore, a term "chemical amplification" means the phenomenon whereby active species produced by the action of one photon causes chemical chain reactions to rapidly



amplify the yield of quantum. Due to this continuous reaction of acid, the concept of chemical amplification was introduced and used.

A chemically amplified resist is divided into a two-component system comprising an acid-labile polymer and a mineral acid producing agent and a three-component system comprising an acid-labile polymer, a  
5 mineral acid producing agent and a matrix resin. In the resist of the prior art, the degradation or the cross-reaction of a light sensitive material occurs directly at the light exposure part, and, when it is developed, a resist image pattern of a positive or negative form is obtained. However,  
10 in the chemically amplified resist, an acid labile polymer or compound is not directly reacted by light exposure, but an acid is produced from the mineral acid producing agent in the light-exposed part, and only a latent image is produced. The produced acid acts as a catalyst for the acid labile polymer in the post-exposure bake (PEB) step, and thus, it causes  
15 the amplification of the reaction and the significant difference in solubility.

The first resist based upon the chemical amplification concept was a resist using a polyhydroxystyrene derivative poly[p-(t-butyloxycarbonyloxy)styrene] (PBOCSt) blocked with t-BOC (tertiary-butoxy carbonyl) group and onium salt as a mineral acid producing agent,  
20 and it is described in American Chemical Society, "Polymers in Electronics", ACS Sym Series, No. 242 by Ito et al. The reason for using the polyhydroxystyrene derivative is as follows: since the novolac phenol resin that was used in the resist of the prior art largely absorbs

deep UV, UV light cannot sufficiently reach the contact surface of the resist substrate. Thus, in the light-exposed part of the resist, chemical changes by light-exposure do not sufficiently occur in the membrane thickness direction, and thus the solubility of the developing liquid becomes irregular. This makes the shape of the section of the resist pattern formed after development triangular. Thus, when the obtained resist pattern is used as an inner etching mask for a substrate, the micro-circuit pattern to be aimed cannot be transcribed. In order to compensate for this, there is a need to change the base polymer, and a polyhydroxystyrene derivative having excellent plasma resistance is known to be suitable.

As examples, a chemically amplified resist comprising poly(p-styreneoxytetrahydropyranol) and an acid producing agent is known by Ueno et al in the 36<sup>th</sup> Japanese Applied Physics Society announcement, 1p-k-7, 1989, and a three component system resist comprising novolac phenol resin, bisphenol-A substituted with t-BOC group and pyrogallol methanesulfonic ester is known from Schlegel in the 37<sup>th</sup> Japanese Applied Physics Society announcement, 28p-ZE-4, 1990. In addition, technologies relating to the preparations of said resists are disclosed in JP patent publication Hei 2-27660, JP patent publication Hei 5-232706, JP patent publication Hei 5-249683, and US patent Nos. 4,491,628 and 5,310,619. However, while such chemically amplified resists have excellent resolutions compared to the resist for g-line and i-line of the prior

art, they are likely to be affected by the surrounding environment, particularly by oxygen, moisture and other trace ingredients around the membrane surface, and it is difficult to form stable micro patterns because a trace amount of acid is produced in the light-exposed part.

5 In addition, MacDonald et al. reported in Proc. SPIE, Vol. 1466. 1991 that trace dimethylaniline contained in the air decreases the activity of the acid produced around the surface of the resist by light exposure, and it produces a layer that hardly melts on the membrane surface, and said hardly-melting layer remains on the surface of the resist pattern after  
10 development treatment. However, this process has the problem that footing is caused by the reaction of the micro pattern with the substrate due to the time delay from the light exposure to the PEB process, and a T-top type pattern is produced by environmental pollution due to the amine ingredient distributed in the air in the process line. Therefore, there is a  
15 need for compensating the PED stability of the resist composition using said compound, and there is a need for a resist composition using a novel base polymer suitable to embody high sensitivity and high resolution at a wavelength of 300 nm or less

In addition, recently, large size integrated circuit tends to use a dry  
20 etching process Said dry process is for increasing integration of semiconductor integrated circuit, and changes the manner of etching on the substrate in the lithography process from wet etching having large side etching of the prior art to dry etching having small side etching. In the dry





The process for synthesizing the monomer having a Z repeat unit comprises two steps. First, group I cyanide comprising sodium cyanide and potassium cyanide is mixed with alkyl alcohol comprising water and ethanol, as shown in Equation 1. To said solution, alkyl styrene comprising 4-chloroalkylstyrene and halogen atoms is slowly introduced and is reacted to synthesize cyanoalkylstyrene. Then, the monomer obtained in Equation 1 is stirred with t-butylacrylate to synthesize 4-(3-cyano-di-1,5-t-butoxycarbonyl-pentyl)styrene (CBCPS) as shown in Equation 2. Wherein, cyanoalkylstyrene and triton non-solution or tetraalkylaminehydroxide solution are dissolved in dioxane, and then, t-butylacrylate is introduced and stirred. After the reaction completes, said mixture is neutralized with an acidic solution and is extracted to synthesize CBCPS.

10

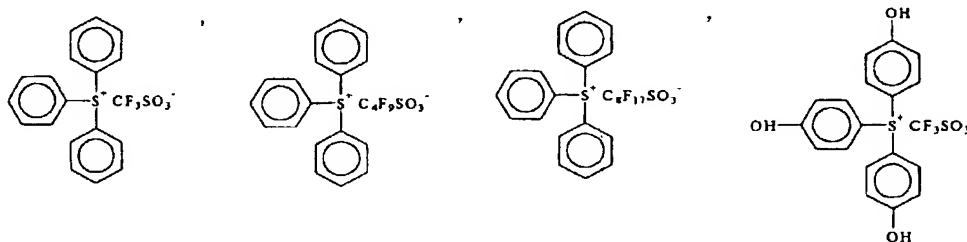
The substitute monomer used in the present invention exhibits sufficient development inhibiting capacity at the non-light-exposed part, and the substitute group is degraded by the action of acid and is dissolved in developing liquid at the light-exposed part.

- 5        The resist composition using the polymer of the present invention comprises (a) a polymer represented by the formula 1, (b) an acid producing agent and (c) an organic solvent.

The resist composition using the polymer of the present invention preferably comprises 1 – 50 wt% of said polymer.

- 10       As the acid producing agent, sulfonium salt, an onium salt such as iodonium, N-iminosulfonate, disulfone, bisarylsulfonyldiazomethane and arylcarbonylarylsulfonyldiazomethane can be used. Preferably, the acid producing agent is contained in the resist composition in an amount of 0.1 to 50 wt%.

- 15       The examples of sulfonium salt include the following compounds but are not limited to them



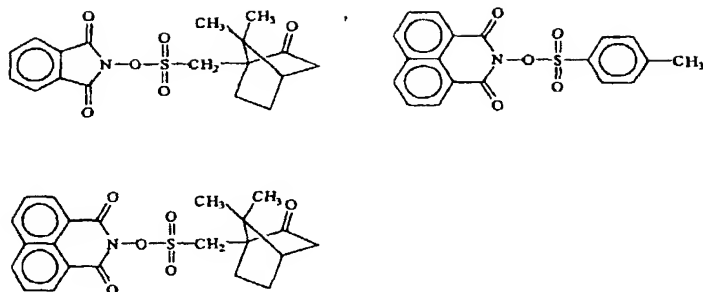




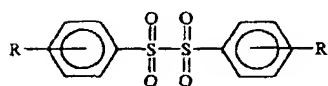


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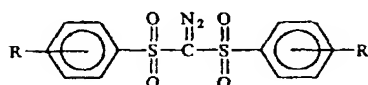


The examples of disulfones include the following compound.



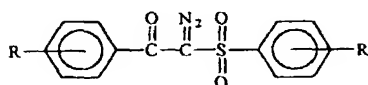
5 (Wherein R is H, -CH<sub>3</sub> or -C(CH<sub>3</sub>)<sub>3</sub>.)

The examples of bisarylsulfonyldiazomethanes include the following compound.



(Wherein R is H, -CH<sub>3</sub> or -C(CH<sub>3</sub>)<sub>3</sub>.)

10 The examples of arylcarbonylarylsulfonyldiazomethanes include the following compound.



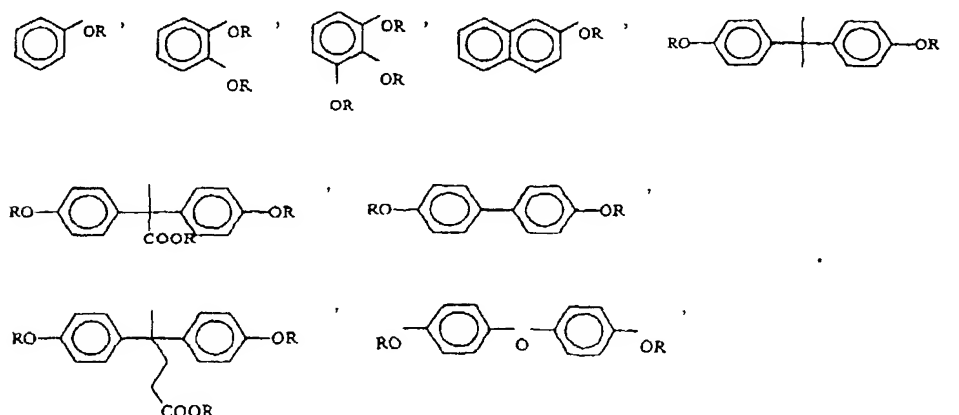
(Wherein R is H, -CH<sub>3</sub> or -C(CH<sub>3</sub>)<sub>3</sub> )

The organic solvent is preferably selected from the group consisting  
15 of ethyleneglycol monoethylether acetate, propyleneglycol monomethylether  
acetate, ethylether acetate, n-butyl acetate, methyl isobutyl ketone, ethyl

lactate, 3-ethoxy-ethylpropionate, 3-methoxy-methylpropionate, diglycol  
monoethylether, 2-heptanone, diacetone alcohol,  $\beta$  - methoxyisobutyric acid  
methylester, propyleneglycol monoethylether, propyleneglycol  
monomethylpropionate, methyl lactate, butyl lactate, ethyl pyruvate,  $\gamma$  -  
5 butyrol lactone, and a mixture thereof Preferably, the organic solvent is  
contained in the resist composition in an amount of 0.1 to 99 wt%.

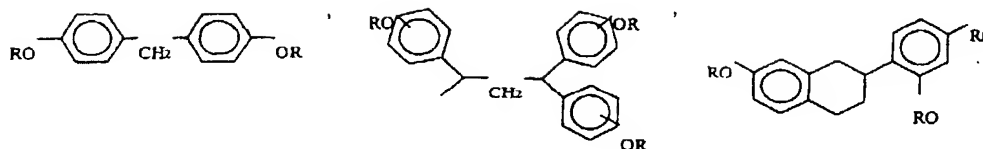
The resist composition using the polymer of the present invention  
may comprise a dissolution inhibitor in order to improve the dissolution  
inhibition of the non-light-exposed part The use of the dissolution inhibitor  
10 makes the difference of solubility of the light-exposed part and non-light-  
exposed part larger and contributes to the improvement of contrast. Such  
dissolution inhibiting additives can be added in the resist composition in an  
amount of 0.1 to 50 wt% based on the weight of the polymer of the present  
invention.

15 The examples of the dissolution inhibitor include the following  
compounds but are not limited to them.



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(Wherein R is a molecule comprising C<sub>1</sub>-C<sub>10</sub> and H and O)

The resist composition using the polymer of the present invention can be applied as follows to obtain a micro-pattern

5 When the resist composition using the polymer of the present invention is formed as a thin layer on a substrate such as a silicone wafer and is treated with a base aqueous solution, the dissolution does not occur because the solubility of the copolymer is low. However, when extreme ultraviolet light is radiated, the resist responds and the acid producing agent  
10 in the resist produces acid, and the development inhibiting substituent causes the degradation of the polymer structure by the action of heat addition in the light-exposed part and the acid is produced again. Consequently, one acid that was produced causes chemical amplification which causes a plurality of acid active degradation. As a result, the  
15 solubility of the polymer largely increases in the light-exposed part, and, when developing with the base aqueous solution, the difference in the solubilities of the light exposed part and non-exposed part appears. Thus, a resist composition having excellent resolution compared to the resist composition using G-rays and I-rays of the prior art can be obtained

20 The present invention will be explained in more detail with reference to the following Examples and Comparative Examples. However, these are

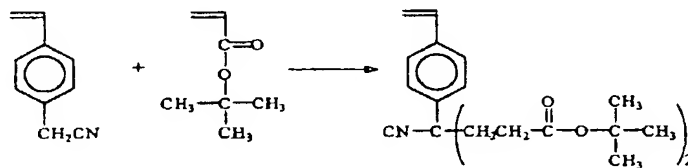


The synthesis of 4-(3-cyano-di-1,5-t-butoxycarbonyl-pentyl)styrene  
(CBCPS)

In a 500 ml 4-opening flask equipped with a stirring bar, 57.28 g of 4-cyanomethylstyrene prepared in the above process and 1.4 g of triton non solution were dissolved in 40 g of dioxane. 102.54 g of t-butylacrylate were slowly added to said solution for 30 minutes while maintaining the temperature of the reactor at 60 °C, and it was reacted for 24 hours while stirring. After the reaction, the reactant was neutralized with a chloride solution, and the neutralized reactant was extracted with 100 g of diethylether and 300 g of water three times, the water layer was extracted with 50 g of diethylether and combined with the organic layer. The separated obtained organic layer was dried with magnesium sulfate for one day, and then the organic solvent was removed using an evaporator. The obtained product was distilled under reduced pressure to remove unreacted material, and it was recrystallized with methanol to obtain light yellow CBCPS in a 60% yield.

Said synthesis was according to the Equation 2.

[Equation 2]



20

The synthesis of the polymer of Formula 1

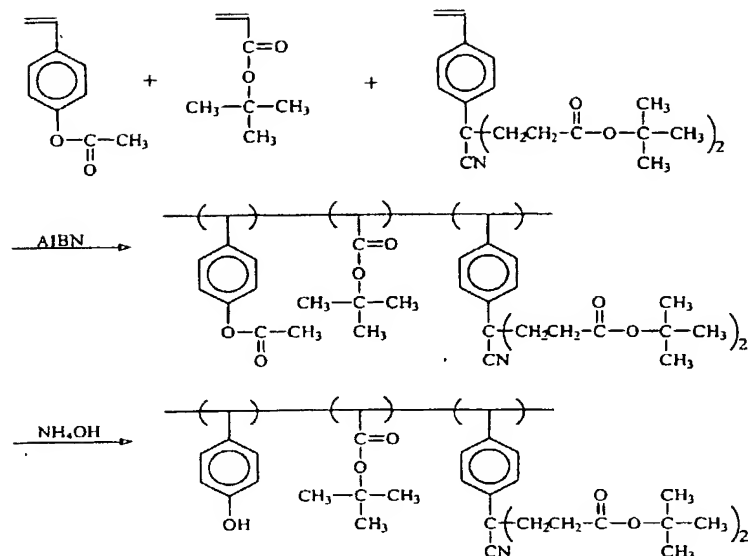
In a 500 ml 4-opening flask equipped with a temperature controlling apparatus and a nitrogen introducing apparatus, 300 ml of THF were introduced and nitrogen was added and it was stirred for 30 minutes. To said reactor, 56.62 g of 4-acetoxystyrene, 9.16 g of t-butylacrylate and 24.14 g of CBCPS prepared in the above process were introduced, 1.21 g of AIBN were added and stirred for 30 minutes under a nitrogen atmosphere while maintaining the temperature at 40 °C, and the temperature of the reactor was then elevated and the reactant was stirred for 24 hours while refluxing. After the completion of the reaction, the temperature was lowered to room temperature and the reactant was deposited in 3 liters of hexane to obtain the precipitates. The obtained precipitates were filtered and rinsed with 2 liters of hexane several times and were vacuum dried. The dried macromolecule was dissolved in 300 ml of methanol in a flask, and 50 ml of 30% NH<sub>4</sub>OH aqueous solution were added and the mixture was slowly stirred, and, after the polymer was completely dissolved, the mixture was additionally stirred for 30 minutes. The solution was deposited in 1.5 liters of water to obtain the precipitates, and the precipitate were filtered and rinsed with 2 liters of pure water and vacuum dried to obtain 58.23 g of polymer of Formula 1.

The above synthesis was according to Equation 3.

[Equation 3]

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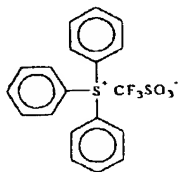


[Examples 1-7]

A chemically amplified resist composition

A chemically amplified resist composition was obtained by using the  
 5 polymer prepared in the above process represented by Formula 1, the  
 compounds represented by Formulae 2 to 6 as acid producing agents, and  
 propyleneglycolmonomethyletheracetate (PGMEA) and ethyl lactate (EL) as  
 solvents in the ratios of Table 1.

[Formula 2]



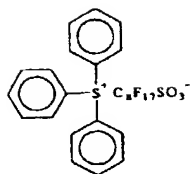
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[Formula 3]

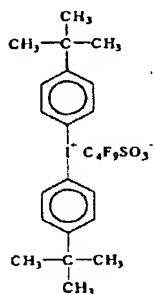


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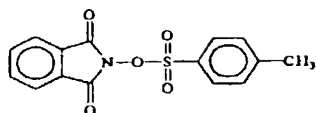


[Formula 4]

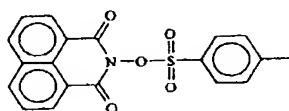


5

[Formula 5]



[Formula 6]



10

Said chemically amplified resist composition was spin coated on  
silicone wafers at 2000 rpm, and was heated to 100 °C for 90 seconds to

form thin layers with thicknesses' as described in Table 1. Micro-pattern masks were mounted on said thin layers, mono wavelengths of 248 nm were radiated, and said layers were heated to 110 °C for 90 seconds to cause the chemical amplification. Then, said layers were developed with a  
5 tetramethylammoniumhydroxide aqueous solution for 60 seconds, and then were rinsed with pure water and dried to embody micro-patterns on wafers.

The relative sensitivities and resolutions of micro-patterns are described in Table 1.

[Comparative Examples 1-4]

10 Chemically amplified resist compositions were prepared by using polyhydroxystyrene blocked with t-BOC(tertiary-butoxy carbonyl) group represented by the formula 7 and EVE (ethyl vinyl ether) represented by the formula 8 as polymers, the compounds represented by the formulae 2-6 as  
acid producing agents, and  
15 propyleneglycolmonomethyletheracetate(PGMEA) and ethyllactate(EL) as solvents, in the ratios of Table 1. Said compositions were spin coated on silicone wafers and were heated to form thin layers, and were chemically amplified to embody micro-patterns, in the same manner as described in the Examples 1 to 7

20 The relative sensitivities and resolutions of the micro-patterns are described in Table 1

[Formula 7]



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Example 4	Formula 1 (100)	Formula 2 (3) Formula 5 (2)	PGMEA (250) EL (300)	0.73	31	0.16
Example 5	Formula 1 (100)	Formula 4 (3) Formula 6 (2)	PGMEA (550)	0.72	27	0.18
Example 6	Formula 1 (100)	Formula 2(3) Formula 6 (2)	PGMEA (550)	0.71	28	0.20
Example 7	Formula 1 (100)	Formula 3 (3) Formula 6 (2)	PGMEA (550)	0.71	33	0.18

Comparative Example 1	Formula 7 (30)	Formula 2 (5)	PGMEA (550)	0.73	35	0.24
Comparative Example 2	Formula 7 (40) Formula 8 (60)	Formula 3 (5)	PGMEA (250) EL (300)	0.73	38	0.24
Comparative Example 3	Formula 7 (100)	Formula 2 (3) Formula 6 (2)	PGMEA (550)	0.74	39	0.30
Comparative Example 4	Formula 7 (100)	Formula 3 (3) Formula 5 (2)	PGMEA (550)	0.72	42	0.28

\* The relative sensitivity in Table 1 means optimum energy (Eop).

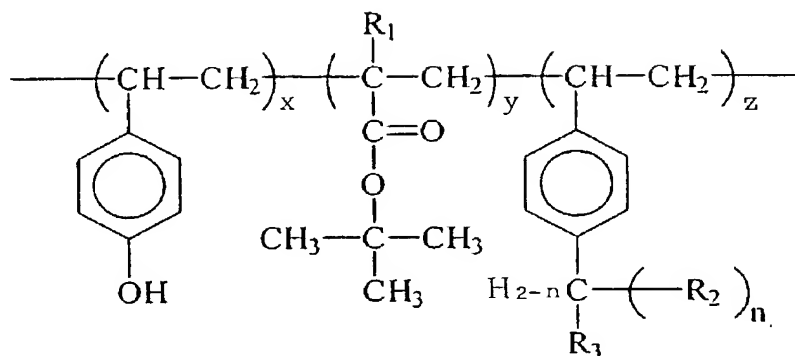
As shown in Table 1, the resist compositions prepared in Examples 1 to 7 of the present invention have resolutions of 0.16 to 0.20  $\mu\text{m}$  which is much excellent compared to the resolutions of 0.24 to 0.30  $\mu\text{m}$  of the compositions prepared in Comparative Examples 1 to 4. In addition, the relative sensitivities of the compositions of Examples are 28 to 30  $\text{mj}/\text{cm}^2$ , which are excellent compared to the relative sensitivities of 35 to 45  $\text{mj}/\text{cm}^2$  of the compositions of Comparative Examples.

10 The chemically amplified resist composition comprising the polymer represented by the Formula 1 can rapidly respond to mono wavelength in a micro-lithography process using extreme ultraviolet light and form micro-patterns of high-resolution on wafers. In addition, it prevents the modification between a resist latent image that occurs by a time delay  
15 between light-exposure and post exposure bake resulting from the environmental effect and a real resist micro-circuit pattern after development, as well as the modification of the surface layer of the resist resulting from the reaction of a mineral acid producing agent and the acid produced by base amine, namely, the formation of T-top type pattern. The resist composition  
20 of the present invention is suitable for the preparations of 256 mega and giga bit DRAM, because it has high resistance against the heat produced by dry etching.

**WHAT IS CLAIMED IS:**

1. A polymer for a chemically amplified resist represented by the following Formula 1:

5 [Formula 1]



Wherein R<sub>1</sub> is hydrogen or methyl, R<sub>2</sub> is hydrogen or CH<sub>2</sub>CH<sub>2</sub>COOC(CH<sub>3</sub>)<sub>3</sub>, R<sub>3</sub> is Cl, Br, hydroxy, cyano, t-butoxy, CH<sub>2</sub>NH, CONH<sub>2</sub>, CH=NH, CH(OH)NH<sub>2</sub> or C(OH)=NH,

10  $x + y + z = 1$ , x is 0.1 – 0.9, y is 0.01 – 0.89, z is 0.01 – 0.89,

n is 1 or 2, and when n is 2, both R<sub>2</sub> are the same.

2. The polymer for a chemically amplified resist according to claim 1, wherein said polymer has a molecular weight of 3,000 to 30,000 and a degree of dispersion of 1.01 to 3.00.

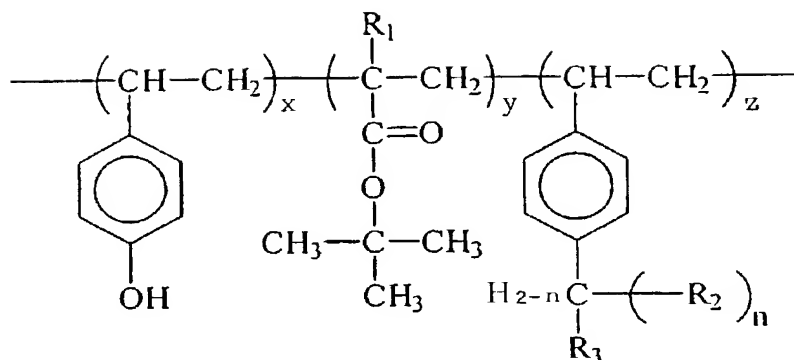
- 15 3. A light sensitive resist composition comprising

a) a polymer represented by the following formula 1:

[Formula 1]

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Wherein  $R_1$  is hydrogen or methyl,  $R_2$  is hydrogen or  $\text{CH}_2\text{CH}_2\text{COOC}(\text{CH}_3)_3$ ,  $R_3$  is Cl, Br, hydroxy, cyano, t-butoxy,  $\text{CH}_2\text{NH}$ ,  $\text{CONH}_2$ ,  $\text{CH}=\text{NH}$ ,  $\text{CH}(\text{OH})\text{NH}_2$  or  $\text{C}(\text{OH})=\text{NH}$ ,

5  $x + y + z = 1$ ,  $x$  is 0.1 – 0.9,  $y$  is 0.01 – 0.89,  $z$  is 0.01 – 0.89,

$n$  is 1 or 2, and when  $n$  is 2, both  $R_2$  are the same.

b) an acid producing agent; and

c) a solvent.

4. A light sensitive resist composition according to claim 3, wherein said  
10 polymer represented by Formula 1 is contained in the composition in an amount of 0.1 to 50 wt%.

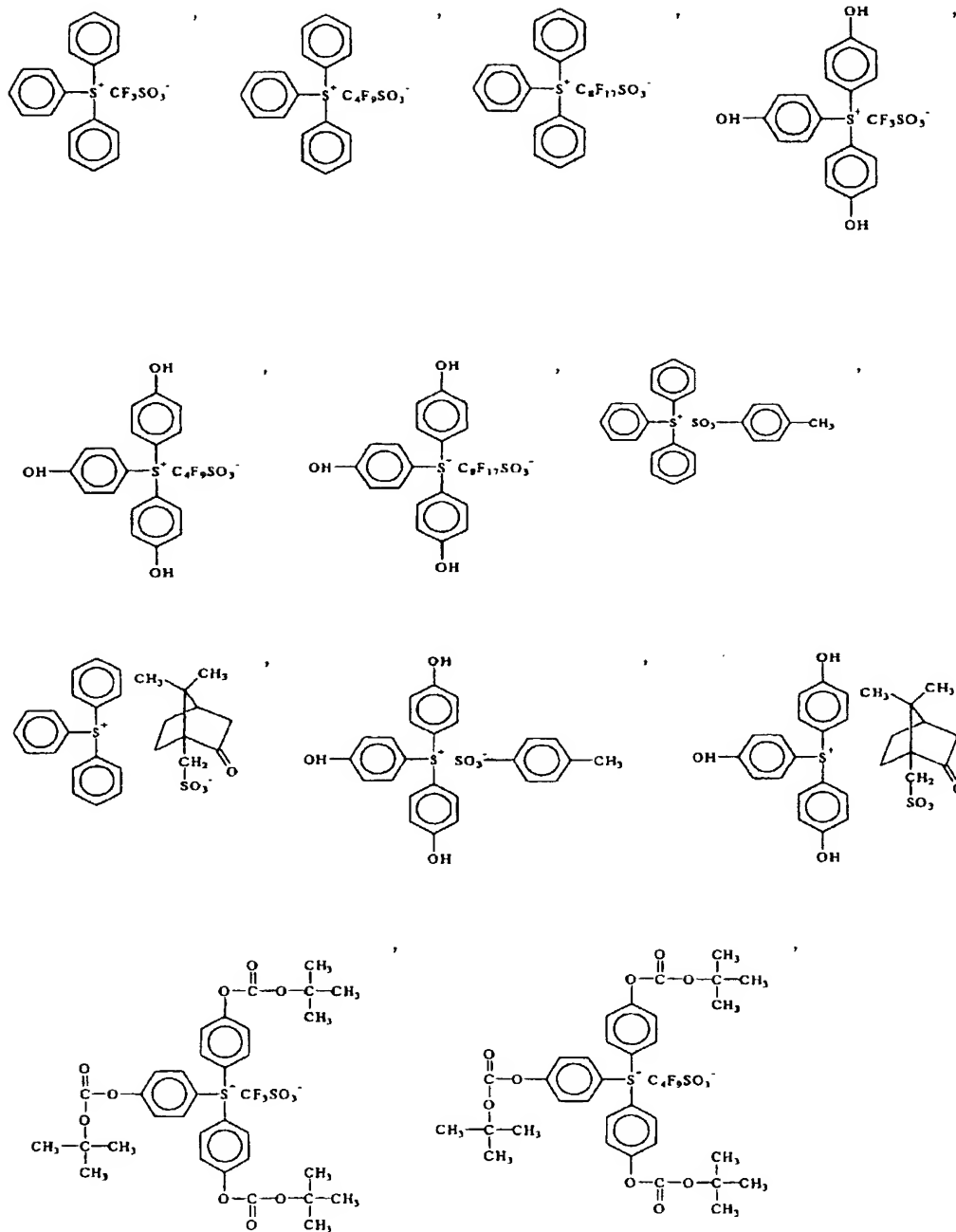
5 A light sensitive resist composition according to claim 3, wherein said b)

acid producing agent is selected from the group consisting of:

sulfonium salt selected from:

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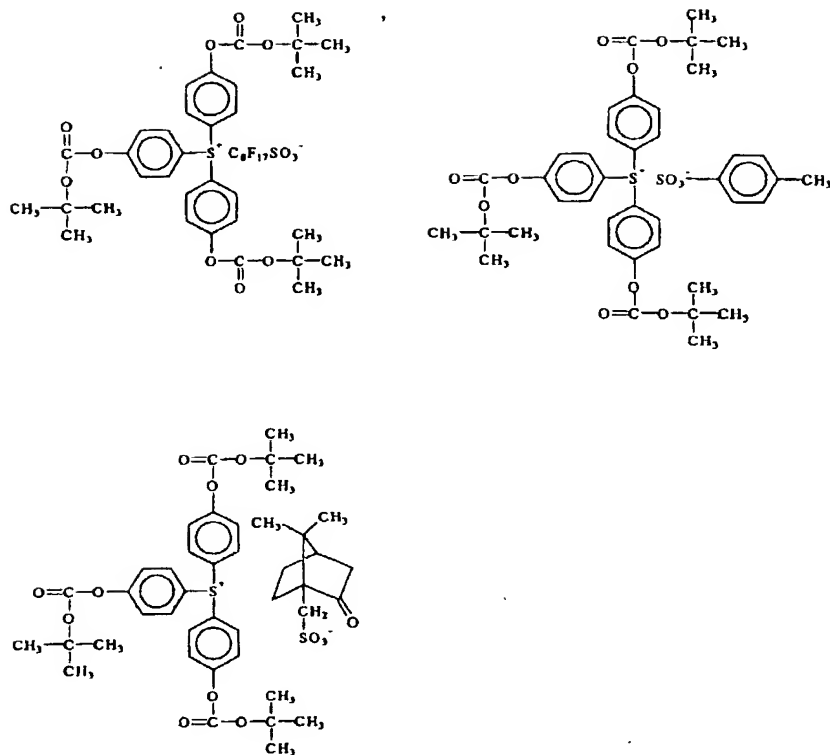
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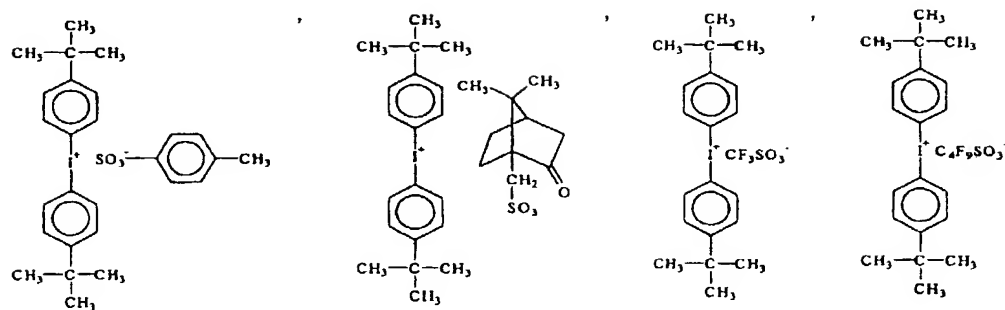


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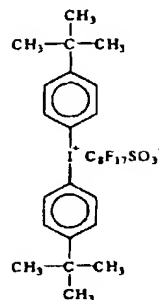


iodonium salt selected from:

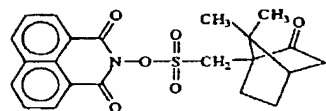
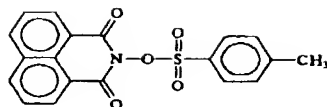
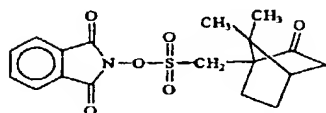
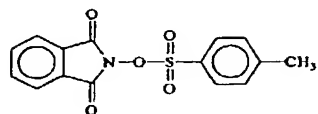


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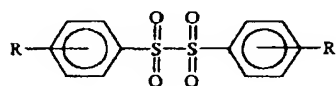


N-iminosulfonates selected from:



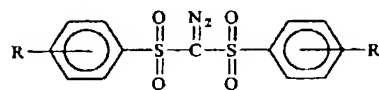
5

disulfonates which is



(Wherein R is H, -CH<sub>3</sub> or -C(CH<sub>3</sub>)<sub>3</sub>)

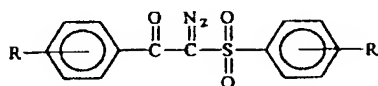
bisarylsulfonyldiazomethane which is



10

(Wherein R is H, -CH<sub>3</sub> or -C(CH<sub>3</sub>)<sub>3</sub>)

arylcarbonylarylsulfonyldiazomethane which is



(Wherein R is H, -CH<sub>3</sub> or -C(CH<sub>3</sub>)<sub>3</sub>),

and a mixture thereof,

- 5 and said acid producing agent is contained in the composition in an amount of 0.1 to 50 wt%.
6. A light sensitive chemically amplified resist composition according to claim 3, wherein said c) solvent is selected from the group consisting of ethyleneglycol monoethylether acetate, propyleneglycol monomethylether acetate, ethylether acetate, n-butyl acetate, methyl isobutyl ketone, ethyl lactate, 3-ethoxy-ethylpropionate, 3-methoxy-methylpropionate, diglycol monoethylether, 2-heptanone, diacetonealcohol,  $\beta$  -methoxyisobutyric acid methyl ester, propyleneglycol monomethylether, propyleneglycol monomethylpropionate, methyl lactate, butyl lactate, ethyl pyruvate,  $\gamma$  -
- 15 butyrol lactone, and a mixture thereof, and said solvent is contained in the composition in an amount of 0.1 to 99 wt%.

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- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: POLYMER FOR CHEMICALLY AMPLIFIED RESIST AND A RESIST COMPOSITION USING THE SAME

(57) Abstract: The present invention relates to a polymer for a chemically amplified resist and a resist composition using the same. The present invention provides a polymer represented by the Formula (1) and a chemically resist composition for extreme ultraviolet light comprising the same. The chemically amplified resist composition comprising the polymer represented by the formula (1) of the present invention responds to mono wavelength in a micro-lithography process and can embody a micro-pattern of high resolution on a substrate.



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**COMBINED DECLARATION  
AND POWER OF ATTORNEY**



(Original, Design, National Stage of PCT, Divisional, Continuation or C-I-P Application)

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name; I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

POLYMER FOR CHEMICALLY AMPLIFIED RESIST AND A RESIST COMPOSITION USING THE  
SAME

This declaration is of the following type:

- ☐ original
- ☐ design
- ☒ national stage of PCT
- ☐ divisional
- ☐ continuation
- ☐ continuation-in-part (C-I-P)

the specification of which: (complete (a), (b), or (c))

- (a) ☐ is attached hereto.
- (b) ☐ was filed as Application Serial No. and was amended on (if applicable).
- (c) ☒ was described and claimed in PCT International Application No. PCT/KR00/00956 filed on August 25, 2000 and was amended on (if applicable).

**Acknowledgement of Review of Papers and Duty of Candor**

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of the subject matter claimed in this application in accordance with Title 37, Code of Federal Regulations § 1.56.

☐ In compliance with this duty there is attached an information disclosure statement. 37 CFR 1.98.

**Priority Claim**

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT International Application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT International Application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application on which priority is claimed

(complete (d) or (e))

- (d) ☐ no such applications have been filed.
- (e) ☒ such applications have been filed as follows:

PRIOR FOREIGN/PCT APPLICATION(S) FILED WITHIN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO SAID APPLICATION				
COUNTRY	APPLICATION NO.	DATE OF FILING (day, month, year)	DATE OF ISSUE (day, month, year)	PRIORITY CLAIMED UNDER 35 USC 119
Korea	1999-37772	September 7, 1999		<input checked="" type="checkbox"/> YES NO <input type="checkbox"/>
				<input type="checkbox"/> YES NO <input type="checkbox"/>
				<input type="checkbox"/> YES NO <input type="checkbox"/>
ALL FOREIGN APPLICATION[S], IF ANY, FILED MORE THAN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO SAID APPLICATION				
				<input type="checkbox"/> YES NO <input type="checkbox"/>
				<input type="checkbox"/> YES NO <input type="checkbox"/>
				<input type="checkbox"/> YES NO <input type="checkbox"/>

**Claim for Benefit of Prior U.S. Provisional Application(s)**

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

Provisional Application Number	Filing Date

**Claim for Benefit of Earlier U.S./PCT Application(s) under 35 U.S.C. 120**  
(complete this part only if this is a divisional, continuation or C-I-P application)

(Application Serial No.)	(Filing Date)	Status (patented, pending, abandoned)

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

BAKER &amp; BOTTS, L L P

FILE NO.: 35043-PCT-USA  
(072944: 0155)

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	DATE 25/02/2002	SIGNATURE OF INVENTOR <u>Yoon Sik Chung</u>		

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